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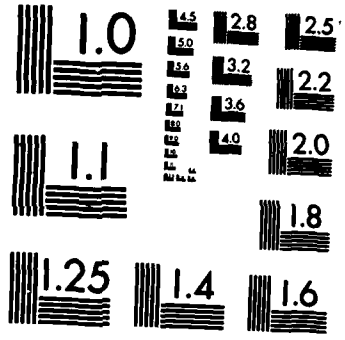

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FINAL TECHNICAL REPORT

CHEMICAL MODIFICATION OF CARBON ELECTRODES

Royce W. Murray, Principal Investigator

Department of Chemistry

University of North Carolina

Chapel Hill, North Carolina

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project had as its objectives the development of chemical and physical pathways to immobilize interesting chemicals on the surfaces of carbon electrodes, to develop surface analytical methods for the characterization and validation of surface immobilization procedures, to study the chemical and electrochemical behavior of the immobilized substances, and to exploit their chemical and electrochemical properties for electrocatalysis in various forms.

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BLOCK 13, KEY WORDS, continued:

multimolecular layer, monomolecular layer, electron transfer, modified electrode, porphyrin, fluorescence, reflectance spectroscopy, spectroelectrochemistry, cobalt, rotated disk electrode, chronoamperometry, kinetics, bromoalkyls, polymers, diodes, cyclic voltammetry, bilayer electrode, rectifier, electrochemical theory, redox polymer, polymer film, viologen, electrochemical theory, plasma polymer, iridium, ascorbic acid, membrane, diffusion, permeation, polymer film, electropolymerization.

FINAL TECHNICAL REPORT

CHEMICAL MODIFICATION OF CARBON ELECTRODES

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This project had as its objectives the development of chemical and physical pathways to immobilize interesting chemicals on the surfaces of carbon electrodes, to develop surface analytical methods for the characterization and validation of surface immobilization procedures, to study the chemical and electrochemical behavior of the immobilized substances, and to exploit their chemical and electrochemical properties for electrocatalysis in various forms. The project began on the theme of covalent bond attachments to carbon surfaces by a variety of strategies to achieve monomolecular layer quantities of attached species. Immobilizations were extended to multimolecular layers of immobilized redox sites when we discovered good electrochemical properties for radiofrequency plasma polymerized vinylferrocene. And finally the project expanded into the first examples of spatially structured electrode surfaces when the rectifying properties of multiple (bilayer) films of redox polymers were demonstrated after having been predicted in an ONR proposal 2 1/2 years before materials were available to make an example. Thus, three discernable thrusts were made, and much was accomplished in each.

To more specifically cite accomplishments under this project, in particular those which opened new ground in the chemically modified electrode area:

** The necessary procedures and chemistry for attachment of monolayers of amine-substituted reagents to surface oxides of vitreous carbon via amide bonds were developed.

** Chemistry for attachment of reactive organosilane reagents was invented enabling immobilization of interesting molecules with the organosilane as a bridge, in submonolaye: to multimolecular layer amounts.

** Amino porphyrins and ferrocenes were attached via both chemistries and their electrochemical reactions demonstrated.

** Extensive surface structural information on quantity, existance of two surface bonds per molecule, average orientation, axial ligation equilibria and kinetics, and stability of immobilized aminoporphyrins was obtained by combinations of cyclic voltammetry, differential pulse voltammetry, fluorescence and reflectance spectroscopies, and X-ray photoelectron spectroscopy experiments.

** Electrocatalytic activity of several metallated forms of the immobilized aminoporphyrins was demonstrated toward dioxygen reduction and alkyl halides, and for the latter, the electrocatalysis kinetics were evaluated as a function of surface quantity from monolayer to multilayer amounts of catalyst.

** Radiofrequency polymerization of vinylferrocene and of vinylpyridine was shown to yield adherant films on carbon surfaces and thereby redox polymer films containing ferrocene and pentachloroiridate respectively were found to exhibit attractive

electrochemical properties.
** An XPS molecular spacer experiment on carbon showed that about 50% of the carboxylic surface oxide functions were separated by the length of an ethylenediamine molecule or less
** It was found that oxide-free carbon surfaces generated by abrasion in absence of air and in the presence of certain vinylsubstituted molecules would stably bind such molecules.
** The first example of a spatially structured coating of redox polymers, the bilayer electrode, was devised by sequentially coating polymeric films of two different electropolymerizable ruthenium complexes on the electrode.
** The bilayer electrode was shown to exhibit the predicted charge rectification at the polymer film/film boundary, in directions predicted from the redox levels of the polymer films, for a series of different bilayers of polymer films.
** A preliminary theory for the rate of switching a bilayer electrode from one state to another was devised; the theory provided an example of control of electron transfer rate between two contacting (polymer) surfaces.

Complete List of Technical Reports

The research results have been reported in a series of publications a listing of which follows in order of the Technical Report each comprised:

J. C. Lennox and R. W. Murray, Chemically Modified Electrodes. VI. Binding and Reversible Electrochemistry of Tetra(Aminophenyl)Porphyrin on Glassy Carbon, J. Electroanal. Chem. 78 (1977) 395. Technical Report #1.

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In press is:

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